

DROPLET SIZE DISTRIBUTIONS AND PHASE EQUILIBRIA WITH IONIC MICROEMULSIONS

J. Theodoor G. Overbeek

Van 't Hoff Laboratory, University of Utrecht
Padualaan 8, 3584 CH Utrecht, The Netherlands

The free energy of droplet type microemulsions containing an ionic surfactant and a non-ionic cosurfactant is formulated on the basis of a curvature dependent interfacial free energy, the pressure difference between the droplets and the continuous medium, and the entropy of mixing of the spherical droplets with the medium. The equilibrium among droplets of various sizes is dealt with via a mass-action approach.

The analysis has been worked out for W/O and for O/W both for saturated (in equilibrium with excess W or O, respectively) and for unsaturated microemulsions.

The calculated free energy of curved electrical double layers forms the basis for understanding the influence of added electrolytes on the curvature dependence of the interfacial tension and on the phase behavior.

Quantitative aspects of the theory are adapted to experimental data obtained for microemulsions consisting of water, NaCl, sodiumdodecylsulphate, pentanol and cyclohexane.

Droplet size distributions and interfacial tensions between the microemulsion and excess water or oil follow from the theoretical treatment. It is stressed that the droplet size distribution is essential for understanding the existence of a finite range of salt concentrations (and cosurfactant concentrations), where a microemulsion may be in equilibrium with both W and O (Winsor III).

INTRODUCTION

In this paper a thermodynamic description of droplet type microemulsions will be used to derive theoretical estimates on the droplet size distribution and on its influence on the phase equilibria of the Winsor type.

Microemulsions are thermodynamically stable mixtures of water (with electrolyte), oil and fairly large amounts of one or more surfactants. A typical example is given by Caljé, Agterof and Vrij¹, based on Hoar and Schulman's² early work, as a mixture of 33% water, 34% toluene, 23% potassium oleate (the "surfactant") and 10% hexanol (the "cosurfactant"). This is a W/O microemulsion containing water droplets of 5 to 10 nm diameter. The large amount of surfactant implies a large internal water-oil interface, and a very large number of water droplets. One might see the stability of a microemulsion as due to the interplay of a small positive interfacial free energy and a small negative free energy of mixing of the droplets with the continuous medium.

When we call the droplet radius, a , and the interfacial tension σ , the interfacial free energy per droplet is equal to $4\pi a^2\sigma$. Since the free energy of mixing per droplet is of the order of kT (Boltzmann constant times temperature) σ must be of the order of $kT/4\pi a^2 \approx 0.01 \text{ mNm}^{-1}$ at room temperature for $a = 5 \text{ nm}$. Such low interfacial tensions cannot be obtained by single chain ionic surfactants. They do cause a considerable decrease of the oil-water interfacial tension, but micelle formation stops that decrease at a value of the order of a few mNm^{-1} . Here the *role of the cosurfactant* is found. It adds its own decrease of interfacial tension to that of the surfactant and may lower the final interfacial tension to practically zero.³

Some surfactants, such as double chain ionic surfactants (AOT, dimethyl-di(long chain)-ammonium salts) or polyethyleneoxide based nonionics do not need a cosurfactant to form microemulsions. They reach ultralow interfacial tension before micelles are formed.

If the interplay between interfacial tension and free energy of mixing were the only factors determining the stability of microemulsions the liquid in the droplets would be expelled, so that smaller and more droplets would be formed (the total interfacial area is virtually constant and is determined by the amount of adsorbed surfactant), with decrease of the free energy. This, however, is contrary to observation, which shows that a certain amount of surfactant solubilizes a finite amount of oil or water or both, depending on the composition of the system, as illustrated in figure 1. Such a behaviour can only be understood if the interface has a preferred curvature and a certain stiffness opposing deviations from that curvature. Introducing interfacial stiffness against bending is equivalent to saying that the interfacial tension depends on the curvature, as will be shown quantitatively later.

MICROEMULSION MODEL AND ITS FREE ENERGY

In the *simplest model* the droplets are spherical and of a single size, in agreement with indications that microemulsions are nearly monodisperse. Most of the ionic surfactant and a comparable amount of the cosurfactant are adsorbed on the droplets; the aqueous regions contain all the water and electrolyte, and a low concentration of the surfactant; the

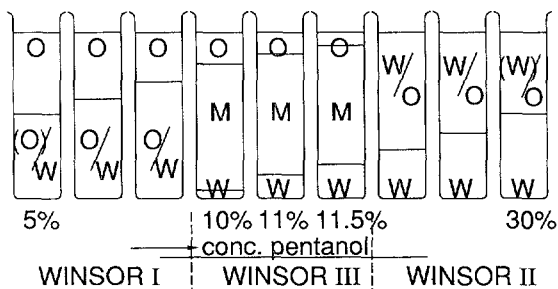


Figure 1. Schematic of phase equilibria in microemulsions. Equal volumes of oil (cyclohexane + pentanol) and water (containing 0.3 M NaCl and 20 gram SDS per l.) spontaneously rearranged into an O/W microemulsion + oil (Winsor I), a W/O microemulsion + water (Winsor II) or in a microemulsion (middle phase, M) in equilibrium with O and W (Winsor III). If 60 instead of 20 gram SDS per l. is taken, the transition region between O/W and W/O is a one-phase microemulsion without excess W or O. For a fixed concentration of pentanol and an increasing salt concentration a similar sequence is found.

oily regions contain all the oil and the non-adsorbed cosurfactant. This model was used in ref.⁴, and explained the change of droplet size with salt- and cosurfactant concentrations and the macroscopic interfacial tension between a W/O microemulsion and excess aqueous phase rather well.

A more refined model takes the droplet size distribution into account and in a further refinement allows the droplet shape to deviate from the spherical and would ultimately include non-droplet type, bicontinuous microemulsions, as must exist in the transition region between O/W and W/O microemulsions, shown in figure 1. Various authors have introduced these refinements. We mention Safran⁵, Borkovec, Eicke and Ricka⁶, Overbeek⁷ and in particular Eriksson and Ljunggren⁸, who used all the above mentioned refinements.

We begin with a W/O microemulsion with spherical droplets of various sizes. We can write its Gibbs free energy in three different but equivalent ways.

$$\begin{aligned}
 G^M &= \sum_i n_i \mu_i = \sum_i n_{im} \mu_i + \sum_j n_{dj} \mu_{dj} \\
 &= \sum_i n_i \mu_i + \sum_j \sigma_j A_j + \sum_j A_j x \Delta p_j + G_{mix}
 \end{aligned} \tag{1}$$

Here G^M is the Gibbs free energy of the microemulsion, n_i is the amount of component i , μ_i its chemical potential, n_{im} is the amount of component i in the continuous medium, n_{dj} is the number of droplets of category, j , and μ_{dj} their chemical potential per droplet. μ_i is the chemical potential of component i at ambient pressure in liquids having the composition of the continuous medium and of the droplets respectively, σ_j is the interfacial tension of the droplets of category, j , and $A_j = 4\pi a_j^2 n_{dj}$ their total area, with a_j being their radius. The Gibbs dividing surface is chosen so as to make water not adsorbed ($\Gamma_w=0$, where Γ_i is the amount of i adsorbed per unit area). Then $A_j x$ is the volume of the layer of surfactant and salt adsorbed and Δp_j the excess pressure in these droplets. Finally G_{mix} is the free energy of mixing of the droplets with the continuous medium.

In the first equality of Equation (1) the microemulsion is considered as being built up from its molecular components (water, salt, oil, surfactant and cosurfactant). The second equality considers the microemulsion as a mixture of the molecular components of the medium (e.g. mainly oil and cosurfactant in a W/O microemulsion) and of the droplets (in this case containing most of the water, salt and surfactant and the cosurfactant, as far as it is adsorbed). The third equality sees the microemulsion formation as making the continuous medium at ambient pressure from its components (without the presence of the droplets), building the droplets, with their adsorption layers from the components at ambient pressure and providing the interfacial free energy, and, finally, mixing the droplets and the medium under decrease of the free energy by an amount G_{mix} (which is negative). The term $\sigma_j A_j$ implicitly takes care of the excess pressure, Δp_j , in the volume, $n_{dj} \times 4\pi a_j^3/3$, of the droplets of type j . But the chemical potentials of the adsorbed salt and surfactant have to be explicitly increased by an amount $\Delta p_j V_i$ per mole of i , since they are in equilibrium with salt and surfactant in the bulk of the droplet and this requires the addition of the term $A_j x \Delta p_j$ with $x = \sum \Gamma_i V_i$ for $i = \text{salt and surfactant}$.

In ref. (4) which treated the case of a monodisperse microemulsion we used an equation for G_{mix} which was valid up to quite high volume fractions of droplets. For a polydisperse system the use of such an equation becomes quite complicated. We therefore limit ourselves here to ideal behavior and write

$$\begin{aligned}
G_{\text{mix}} &= \sum n_{\text{dj}} kT \left(\ln \frac{n_{\text{dj}}}{V^{\text{M}}} - 1 + \ln \left(\frac{\pi}{12n_{\text{j}}} \right)^{3/2} v_{\text{dj}} \right) \\
&= \sum n_{\text{dj}} kT \left(\ln \frac{4\pi a_{\text{j}}^3}{3V^{\text{M}}} n_{\text{dj}} - 1 + \frac{3}{2} \ln \frac{v_{\text{w}}}{16a_{\text{j}}^3} \right)
\end{aligned} \tag{2}$$

Here V^{M} is the volume of the microemulsion, v_{dj} the volume of one droplet of type j , n_{j} the number of molecules in such a droplet and v_{w} the volume of one molecule in the droplet, for which we take the volume per water molecule in a W/O microemulsion. The term $\ln v_{\text{dj}} + 1,5 \ln(\pi/12n_{\text{j}})$ is due to Reiss⁹ and describes the contribution caused by the breaking up of a macroscopic phase into droplets of the same composition. For criticism on the use of the Reiss term, see ref. (8).

THE DROPLET SIZE DISTRIBUTION

The difference between μ_{im} and μ'_{im} in Equation (1) is due to the presence of the droplets and for an ideally dilute solution is given by (cf. ref. 7)

$$\sum_i n_{\text{im}} \mu_i = \sum_i n_{\text{im}} \mu'_i - \sum_j n_{\text{dj}} kT \tag{3}$$

Using this expression to eliminate the contribution of the continuous medium from the second and third equalities of Equation (1) we obtain the following explicit expression for the chemical potential of the droplets, μ_{dj} .

$$\mu_{\text{dj}} = \sum_i \frac{n_{\text{ij}} \mu_i}{n_{\text{dj}}} + 4\pi a_{\text{j}}^2 (\sigma_{\text{j}} + x\Delta p_{\text{j}}) + kT \left(\ln \frac{4\pi a_{\text{j}}^3}{3V^{\text{M}}} n_{\text{dj}} + \frac{3}{2} \ln \frac{v_{\text{w}}}{16a_{\text{j}}^3} \right) \tag{4}$$

μ_{dj} can also be written as the sum of the chemical potentials of the constituent molecular components (law of mass action) and thus

$$\mu_{\text{dj}} = \sum_i \frac{n_{\text{ij}}}{n_{\text{dj}}} \mu_i \tag{5}$$

where n_{ij} is the amount of i in all the droplets of type j . After eliminating μ_{dj} from Equations (4) and (5) the resulting expression can be solved for the concentration of droplets of category j . This leads to

$$\ln \frac{n_{\text{dj}}}{V^{\text{M}}} = \ln \frac{48a_{\text{j}}^{3/2}}{\pi v_{\text{w}}^{3/2}} - \frac{4\pi a_{\text{j}}^2}{kT} (\sigma_{\text{j}} + x\Delta p_{\text{j}}) - \sum_i \frac{n_{\text{ij}}}{n_{\text{dj}}} \frac{\mu_i - \mu_i}{kT} \tag{6}$$

The sum over i in the last term does not contain contributions of the components adsorbed from the continuous medium since according to Equation (3) these contributions are proportional to the concentration of droplets and thus may be neglected for small volume

fractions. Furthermore this term is zero for microemulsions in equilibrium with excess internal phase (O/W+O = Winsor I, W/O+W = Winsor II) since droplets and external phase have the same composition and thus μ_i' has the same value as the chemical potential in the external phase and this again is equal to μ_i in the microemulsion as a whole.

Unsaturated microemulsions spontaneously take up liquid with the composition of the droplets and thus, for them, $\mu_i' - \mu_i$ is positive. The difference between μ_i' and μ_i is due to two effects, the pressure difference Δp_j between droplets and continuous medium and the fact that the droplets are dispersed in the medium, making μ_i smaller for smaller droplet concentration.

We showed in ref. (4) that both effects are proportional to V_i the molar volume of i and that $(\mu_i' - \mu_i)/V_i$ does not depend on the component i . Assuming that this remains true when the droplets are not all of the same size, we may write:

$$\sum_i \frac{n_{ij}}{n_{dj}} \frac{\mu_i' - \mu_i}{kT} = \sum_i \frac{n_{ij} \bar{V}_i}{n_{dj}} \cdot \frac{\mu_i' - \mu_i}{\bar{V}_i kT} = \left(\frac{4}{3} \pi a_j^3 + 4 \pi a_j^2 x \right) \text{MU} \quad (7)$$

with $\text{MU} = (\mu_i' - \mu_i)/\bar{V}_i kT$ being positive for unsaturated and zero for saturated microemulsions.

We now need to know how σ_j and Δp_j depend on a_j . Because, as mentioned earlier, σ depends on a , the pressure excess, Δp , inside a droplet is not simply given by the Laplace expression, $\Delta p = 2\sigma/a$. Consider therefore a droplet with radius a_j , which is increased to $a_j + da$. The work done by the excess pressure is $4\pi a_j^2 \Delta p_j da$. This is equal to the increase in interfacial free energy. Thus:

$$4\pi a_j^2 \Delta p_j da = d(4\pi a_j^2 \sigma_j) = 4\pi a_j^2 \frac{\partial \sigma_j}{\partial a} da + 8\pi a_j \sigma_j da$$

or,

$$\Delta p_j = \frac{2\sigma_j}{a_j} + \frac{\partial \sigma_j}{\partial a} = \frac{2\sigma_j}{a_j} - \frac{2}{a_j^2} \frac{\partial \sigma_j}{\partial (2/a)} = \frac{2\sigma_j}{a_j} - \frac{2c_j}{a_j^2} \quad (8)$$

where the curvature $2/a$ has been introduced in preference to the radius a and the *bending stress coefficient* c has been defined as

$$c = \left(\frac{\partial \sigma}{\partial (2/a)} \right)_{T,p,\text{chemic.composit.}} \quad (9)$$

Interfacial Tension vs. Curvature

Two opposing effects influence the curvature of the interface and its resistance against changes of curvature. At the high adsorptions that occur in microemulsions the hydrocarbon tails of the surfactant and cosurfactant molecules repel one another, tending to curve the surface around the water side. At the water side the counterions of the adsorbed surfactant ions repel one another and try to curve the surface around the oil side. This mutual repulsion of counterions can be weakened by adding electrolyte to the aqueous phase and thus increase of salt concentration promotes W/O, decrease of salt concentration promotes O/W. Similarly increase of cosurfactant concentration in the oil phase promotes W/O by increase of the repulsion among the tails and also by forcing some ionic surfactants out of the adsorption layer, thus weakening the repulsion in the electric double layer.

We understand, at least qualitatively, that the concentrations of salt and of cosurfactant

affect the average droplet radius and ultimately the nature (O/W or W/O) of the microemulsion. On the other hand, a higher concentration of the ionic surfactant simply creates more surface, leading to more particles and a higher volume fraction, but it has only a minor effect on the average particle size.

When we plot the expected contributions of the hydrocarbon tails and the electric double layer to the interfacial tension versus the curvature we obtain figure 2, in which we see that the interfacial tension has a more or less parabolic form with a minimum for a certain curvature (chosen positive for W/O) and the bending stress coefficient c increases monotonically from low values for O/W to high values for W/O.

The contribution of the electrical double layer to σ and to c can be calculated quantitatively for curved surfaces on the basis of the Poisson-Boltzmann equation, as has been shown in detail in ref. (4). These contributions depend on the surface charge density (thus on the adsorption of the ionic surfactant) and on the electrolyte content, which determines the thickness of the double layer. Although surfactant and cosurfactant are adsorbed to saturation at a planar interface (i.e. their adsorption densities hardly depend on their own concentrations) within the regions of interest, the adsorption densities may depend on the curvature. The simple assumption that constant packing occurs at a small distance, ξ , on the oil side of the Gibbs surface ($\Gamma_w=0$) with $\xi \approx 0.3$ nm (choice not critical) has led to good agreement between calculated droplet radii and interfacial tensions with the corresponding experimental values over a wide range of salt and cosurfactant concentrations. Over that range the contribution of the hydrocarbon tails turned out to be virtually constant. See ref. (4) and this paper after Equation (15).

To a good approximation c and σ can be represented as

$$c = -b + \frac{d}{a} \quad (10)$$

$$\sigma = \sigma_{\infty} - \frac{2b}{a} + \frac{d}{a^2} \quad (11)$$

where b and d are constants. b is positive for W/O conditions, of the order of 10^{-12} N and decreases with decreasing concentrations of electrolyte and cosurfactant to become negative for O/W conditions. See also Equation (16). d is as good as independent of salt and cosurfactant concentrations and is of the order of $2.5-3$ $kT \sim 10^{-20}$ J. σ_{∞} is small to very small and is automatically adapted by small changes in the free surfactant concentration to the total volume (in essence the amount of water) and the interfacial area (determined by the amount of surfactant) of the droplets. It is somewhat paradoxical that a microemulsion cannot exist unless the interfacial tension is very low, but the nature (O/W or W/O) and droplet size of the microemulsion are mainly determined by the bending stress parameter c (through b and d in our approximate Equation (10)), whereas the precise value of the interfacial tension is adaptable.

If an excess of water is offered it is not taken up in the microemulsion, because that would increase the average volume of the droplets, decrease their number and thus would lead to an unfavorable increase of the free energy of mixing.

With the use of Equations (7), (8), (10) and (11) the Equation (6) for the droplet size distribution can be transformed into a form (12) that can be easily used for computations.

$$\ln \frac{n_{dj}}{V^M} = \ln \frac{48a_j^{3/2}}{\pi v_w^{3/2}} - \frac{4\pi d - 8\pi x b}{kT} + \frac{8\pi a_j}{kT} (b - x\sigma_{\infty}) - \frac{4\pi a_j^2}{kT} \sigma_{\infty} - \left(\frac{4\pi a_j^3}{3} + 4\pi a_j^2 x \right) \text{MU} \quad (12)$$

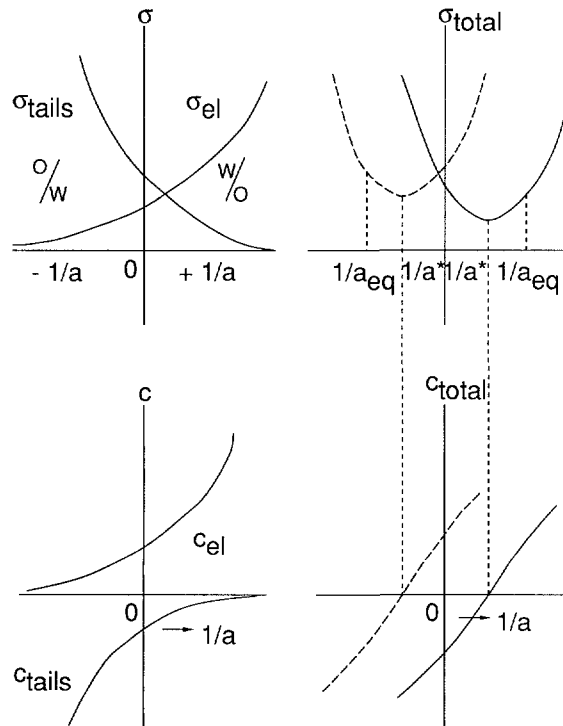


Figure 2. Curves showing, schematically, how the interfacial tension, σ , and the bending stress parameter, $c = \partial\sigma/\partial(2/a)$, are built up from contributions of the hydrocarbon tails of the adsorbed surfactants and of the electrical double layer. The abscissa, the curvature, $1/a$, is counted positive, when the interface curves around the water side, negative when it curves around the oil side. The radius for which $c=0$ is called the natural radius a^* . The actual droplet radius in microemulsions is in absolute value smaller than a^* , since that provides a higher entropy. In the curves for σ (total) and c (total) dotted lines refer to O/W, drawn lines to W/O microemulsions.

As mentioned before $MU = 0$ for Winsor II (and also for Winsor I) equilibria, and is positive and, being an inverse molecular volume (see Equation (7)), is of the order of 0.1 nm^{-3} for unsaturated microemulsions.

The Categories, j

We still have to specify how the categories, j, of the droplets are chosen. A simple choice, also made in ref. (7), is to make j equal to the number of adsorbed surfactant molecules per droplet or

$$j = 4\pi a_j^2 \Gamma_{sa,j} N_{Av} = 4\pi(a_j + \xi)^2 \Gamma_{sa} N_{Av} \quad (13)$$

where N_{Av} is Avogadro's constant and ξ , as mentioned before, the distance between the Gibbs surface, where $\Gamma_w=0$, and the surface of constant packing, slightly displaced towards the oil side. Γ_{sa} is the amount adsorbed per unit area of a flat interface. The choice (13) for j assumes that for each value of j the numbers of water and salt molecules in the droplet are fixed. Another choice for j would take into account that for a fixed number of surfactant molecules the number of water molecules and thus a_j might vary to some extent (see ref. (6)). The number of categories would increase still more drastically, if changes in shape of the droplets are taken into account. In the analysis by Eriksson and Ljunggren this increases the number of categories to such an extent that the Reiss term in Equation (2) and thus in Equation (12) may be omitted.

Oil-in-Water Microemulsions

In order to complete our analysis we have to adapt Equations (12) and (13) to the O/W case. In Equation (12) the following changes have to be made.

1. $(a_j/v_w)^{3/2}$, which stems from the Reiss term (see Equation (2) and ref. (9)) has to be replaced by $(a_j/v_o)^{3/2}(1-3(x+y)/a_j)^{1/2}$, since the volume of oil in a droplet is equal to $4/3 \pi a_j^3$ minus the adsorbed amounts of surfactant, cosurfactant and salt $= 4/3 \pi a_j^3 - 4\pi a_j^2(x+y)$, where $y = \Gamma_{co}V_{co}$. v_o is the average volume of the oil molecules and the cosurfactant molecules that are not adsorbed. As for the W/O case the solubility of the cosurfactant in the aqueous phase is neglected for simplicity.
2. The signs of the three terms containing x in Equation (12) have to be changed, since the volume of the adsorbed surfactant layer sits inside, rather than outside of the Gibbs surface with radius a_j .
3. For similar reasons $+\xi$ in Equation (13) has to be changed to $-\xi$.
4. The Equations (10) and (11) for c and σ may remain unchanged, but this implies that b has changed sign and is counted positive for O/W type curvature.

Consequently we obtain for O/W microemulsions

$$\ln \frac{n_{dj}}{V^M} (\text{O/W}) = \ln \frac{48}{\pi} \left(\frac{a_j}{v_o} \right)^{3/2} \left(1 - 3 \frac{x+y}{a_j} \right)^{1/2} - \frac{4\pi d + 8\pi x b}{kT} + \frac{8\pi a_j}{kT} (b + x\sigma_\infty) - \frac{4\pi a_j^2}{kT} \sigma_\infty - \left(\frac{4\pi a_j^3}{3} - 4\pi a_j^2 x \right) MU \quad (14)$$

$$j(\text{O/W}) = 4\pi (a_j - \xi)^2 \Gamma_{sa} N_{Av} \quad (15)$$

In order to prepare Equations (12)-(15) for computations the values of the parameters have to be specified. We mainly use the data of ref. (4), which refer to systems consisting

of water, NaCl, sodiumdodecylsulphate (SDS), pentanol as the cosurfactant and cyclohexane as the oil. For this system $v_w = 18 \text{ cm}^3/N_{Av}$; $v_o(\text{cyclohexane} + \text{pentanol}) = 108 \text{ cm}^3/N_{Av}$; $d = 2.8 \text{ kT}$; $x = y = 0.4 \text{ nm}$; $\xi = 0.3 \text{ nm}$. For other systems the numerical values may be somewhat different, but general principles and orders of magnitude remain unchanged. The electrical contribution to b can be calculated from double layer theory. The contribution of the hydrocarbon tails showed itself to be independent of salt and cosurfactant concentrations (0.1 - 0.4 M NaCl, 1-20% pentanol in cyclohexane). The conditions where O/W goes over into W/O and where $b = 0$ were taken from experiments (0.15 M NaCl for 19% w/w pentanol in 81% cyclohexane).

The electrical contribution to b is found from

$$b_{el} = 4 \left(\frac{kT}{e} \right)^2 \epsilon_r \epsilon_o \left\{ \ln \left(\frac{q+1}{2} \right) + \kappa \xi p \ln(p+q) \right\} \quad (16)$$

where ϵ_r is the dielectric constant of water, ϵ_o the permittivity of the vacuum, κ is the inverse Debye length, $p = \sqrt{(q^2-1)} = (e/kT) \cdot (\Gamma_{sa} F / (2\epsilon_r \epsilon_o \kappa))$ varying roughly between 2 and 4, with F = Faraday constant and Γ_{sa} the adsorption of the surfactant at a flat interface, determined from the water-oil interfacial tension vs conc of surfactant³ (below the c.m.c.). For 19% pentanol-81% cyclohexane values of b for a range of NaCl concentrations are shown in Table I.

Then for MU = zero, i.e. for Winsor I or II equilibria σ_∞ is found by trial and error until the desired interfacial area, i.e. the chosen amount of surfactant or the desired volume fraction is obtained. For unsaturated microemulsions both MU and σ_∞ have to be adapted until the desired degree of unsaturation and the desired interfacial area are obtained. Useful first guesses for MU and σ_∞ can be obtained from the equations for monodisperse microemulsions, as given in ref. (4). They lead to:

$$\sigma_\infty = \frac{bn}{\langle a_1 \rangle} (4-3n) + \frac{3n^2 kT}{16\pi \langle a_1 \rangle^2} (1-14 \ln n) \quad (17)$$

$$\text{MU} = \frac{6(n-1)bn^2}{\langle a_1 \rangle^2 kT} + \frac{21 n^3 \ln n}{4\pi \langle a_1 \rangle^3} \quad (18)$$

In these equations $\langle a_1 \rangle$ is the average radius ($\sum n_d a_j^3 / \sum n_d a_j^2$) of the saturated microemulsion with the same amount of surfactant as the unsaturated one and n is the degree of unsaturation ($= (\sum n_d a_j^3)_{\text{sat}} / (\sum n_d a_j^3)_{\text{unsat}}$).

Interfacial Tension Between Microemulsion and Excess Water (or Oil)

So far we have considered the interfacial tension, σ , between droplets and continuous medium and σ_∞ the value that interfacial tension would have for a flat interface. In the Winsor I and II equilibria the macroscopic interfacial tension between the microemulsion and oil or water respectively (which we call γ_{MO} and γ_{MW}) are close to, but not exactly equal to σ_∞ . The difference is due to the fact that for σ_∞ the phases are at chemical potentials, μ'_{im} for the medium and at $\mu'_{i,dr}$ for the droplet components, but at $\mu_{im} \neq \mu'_{im}$ and at $\mu_{i,eq liq} = \mu'_{i,dr}$ for γ_{MO} and γ_{MW} .

Table I. Values of Γ_{sa} (SDS in saturation adsorption), b_{el} and b for the interface (19% w/w pentanol + 81% cyclohexane)/(water+0.10-0.30 M NaCl) at 25 °C (From ref. 4).

conc. NaCl	0.10M	0.12M	0.14M	0.146M	0.148M	0.15M		
$\Gamma_{sa}/\mu\text{mol m}^{-2}$	1.565	1.608	1.644	1.6525	1.657	1.660		
$b_{el}(\text{eq.16})/10^{-12}\text{N}$	6.66323	6.56137	6.46701	6.44137	6.43172	6.42237		
$\frac{b(\text{O/W})}{10^{-12}\text{N}} = \frac{b_{el}-b_{el}(0.15\text{M})}{10^{-12}\text{N}}$	0.2409	0.1390	0.0446	0.01900	0.00935	0		
conc. NaCl	0.15M	0.1515M	0.153M	0.16M	0.18M	0.20M	0.25M	0.30M
$\Gamma_{sa}/\mu\text{mol m}^{-2}$	1.660	1.66225	1.6645	1.675	1.705	1.73	1.78	1.82
$b_{el}(\text{eq.16})/10^{-12}\text{N}$	6.42237	6.41554	6.40888	6.37978	6.31289	6.24096	6.06662	5.91336
$\frac{b(\text{W/O})}{10^{-12}\text{N}} = \frac{b_{el}(0.15\text{M})-b_{el}}{10^{-12}\text{N}}$	0	0.00684	0.0135	0.0426	0.1095	0.1814	0.3558	0.5090

Thus we have

$$\begin{aligned} \gamma_{\text{MO}}(\text{or } \gamma_{\text{MW}}) &= \sigma_{\infty} + \left(\sum_i \int_{\mu_m}^{\mu_m} \frac{\partial \sigma}{\partial \mu_i} d\mu_i \right)_{\text{medium}} \\ &= \sigma_{\infty} - \left(\sum_i \Gamma_i (\mu_i - \mu_i^0) \right)_{\text{medium}} = \sigma_{\infty} + \left(\sum_i \Gamma_i \bar{V}_i \right)_{\text{medium}} \cdot \sum \frac{n_{dj} kT}{V^M}. \quad (19) \end{aligned}$$

$$\text{So } \gamma_{\text{MO}} = \sigma_{\infty}(\text{O/W}) + x\Pi, \text{ and } \gamma_{\text{MW}} = \sigma_{\infty}(\text{W/O}) - x\Pi \quad (20)$$

where Π is the osmotic pressure that would be caused by the droplets and x has the meaning of $\sum_i \Gamma_i \bar{V}_i$ for the components of the aqueous liquid.

Here the fact is used that in the Gibbs model of the interface

$$\left(\sum_i \Gamma_i \bar{V}_i \right)_{\text{all comp.}} = \left(\sum_i \Gamma_i \bar{V}_i \right)_{\text{medium}} + \left(\sum_i \Gamma_i \bar{V}_i \right)_{\text{droplets}} = 0 \quad (21)$$

RESULTS AND DISCUSSION

In figures 3 and 4 we show a few droplet size distributions, plotted as number of droplets j (n_{dj}/V^M) against a (which is nearly proportional to \sqrt{j} ; see Equation (13)). The size distributions are fairly wide; they become relatively narrower with decreasing average droplet size (see also ref. (7)). The widths of the distributions agree in order of magnitude with the meagre experimental data (e.g. from SAXS measurements) that are available.

In figure 5 we have plotted the average droplet radius ($\Sigma n_{dj}a_j^3/\Sigma n_{dj}a_j^2$) and the interfacial tension γ_{MW} or γ_{MO} resp. (Equation (20)) against the concentration of NaCl in the aqueous medium. All these points refer to a volume fraction of the droplets ($\Sigma n_{dj}4\pi a_j^3/3V^M$) of 2%. With increasing volume fraction both $\langle a_j \rangle$ and γ_{MW} (or γ_{MO}) increase moderately, somewhat more in the theoretical estimates than in the experiments.

It can be seen that there is a narrow range of NaCl concentrations (about 0.145M - 0.154M) where both Winsor I (O/W+O) and Winsor II (W/O+W) equilibria exist, in qualitative agreement with the finite range of salt concentrations where Winsor III equilibria (microemulsion in equilibrium with both water and oil) exist. This overlap of the Winsor I and II coexistence regions is directly due to the assumption that the microemulsions are not monodisperse. For monodisperse microemulsions the NaCl concentration where $b = 0$ (in our case 0.15M) separates Winsor I from Winsor II. Then at 0.15 M NaCl $a(W/O)$ and $a(O/W)$ would both go to infinity and the corresponding interfacial tensions (γ_{MW} and γ_{MO}) would go to zero.

The existence of both W/O and O/W microemulsions at the same salt (and cosurfactant) concentration can be pushed one step further. It can be shown that the same overall composition can be described as a W/O microemulsion (which may be in equilibrium with W) or as an O/W microemulsion (possibly in equilibrium with oil). To that purpose we assume for simplicity that Equations (12) and (14) continue to be valid for high droplet concentrations.

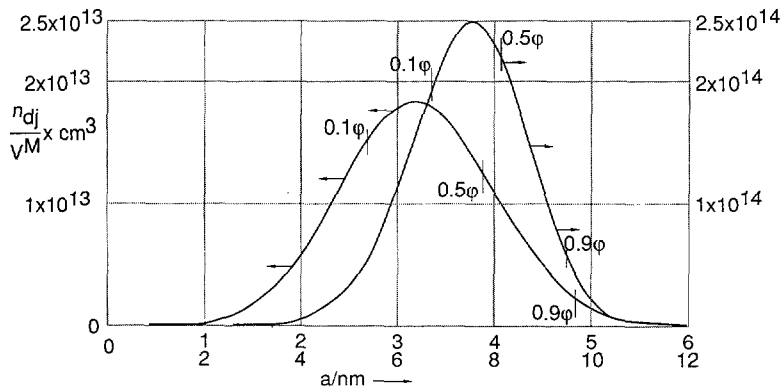


Figure 3. Droplet size distributions. Number of droplets of category j per cm^3 against the droplet radius, a . The lower and relatively broader curve refers to a saturated microemulsion (W/O+W; 0.25 M NaCl; 19% pentanol+81% cyclohexane; $\phi = \Sigma(4\pi a_j^3 n_{dj})/3V^M = 2\%$; 0.01554 mol SDS adsorbed per liter microemulsion). Parameters b and d have been adapted to a switch over from O/W to W/O at 0.15 M NaCl and an average droplet radius of 6 nm at 0.30 M NaCl. The higher and narrower curve refers to a half saturated microemulsion containing the same amount of adsorbed SDS, but $\phi = 1\%$. The vertical lines marked 0.1ϕ , 0.5ϕ and 0.9ϕ indicate the droplet radius below which the particles contain 0.1, 0.5 or 0.9, respectively, of the total droplet volume.

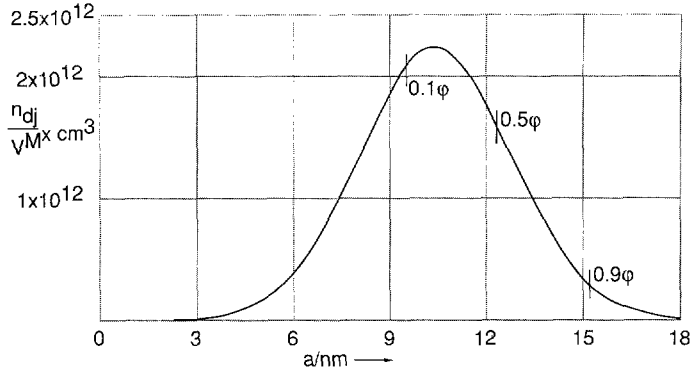


Figure 4. Droplet size distribution for a saturated (Winsor I) O/W microemulsion at 0.1 M NaCl; $\phi=2\%$; 0.007467 mol SDS adsorbed per liter microemulsion. One has to realize that Equation (14) does not allow the droplet radius a_j to be smaller than $3(x+y) = 2.4$ nm, because the adsorbed surfactant and cosurfactant are located inside the radius, a_j .

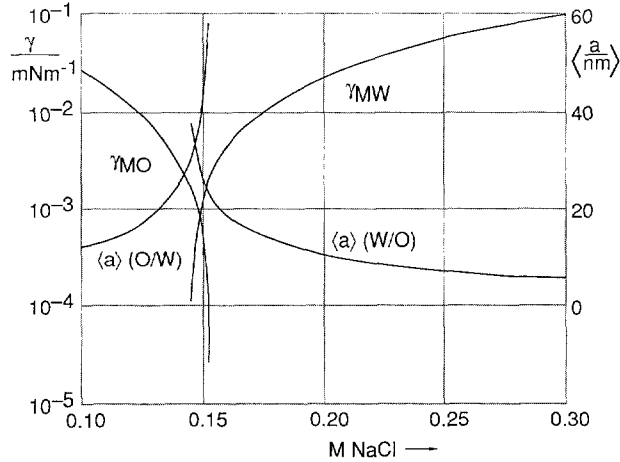


Figure 5. Average droplet radii and interfacial tensions in (O/W+O) and in (W/O+W) equilibria at $\phi=2\%$. Parameters are chosen as mentioned in Figure 3 and in Table I. Note the range of NaCl concentrations around 0.15 M where O/W and W/O can both exist.

Then we adapt at $MU = 0$ the two σ_∞ 's so that

$$\phi(O/W) + \phi(W/O) = \left(\sum \frac{n_{dj}}{V^M} \cdot \frac{4}{3} \pi a_j^3 \right)_{O/W} + \left(\sum \frac{n_{dj}}{V^M} \cdot \frac{4}{3} \pi a_j^3 \right)_{W/O} = 1 \quad (22)$$

and

$$\left(\sum j n_{dj} \right)_{O/W} = \left(\sum j n_{dj} \right)_{W/O} \quad (23)$$

the latter condition guaranteeing that the two microemulsions contain the same amount of ionic surfactant.

Figure 6 and Table II present the results. From 0.1472 M NaCl to 0.1515 M NaCl the above mentioned situation can be realized with average droplet radii between 36 and 95 nm and interfacial tensions from 7×10^{-6} to 8.1×10^{-4} mNm⁻¹. We may consider these situations, where the same overall composition can be described just as well as O/W or as W/O in equilibrium with O or W respectively as a model for the middle type microemulsion, switching over rapidly from O/W to W/O and vice versa, and thus in practice as bicontinuous.

This, of course, does not detract from the desirability of developing a more direct model for the middle type microemulsion and for further considering the quantitative influence of refinements of the model, such as allowing the number of water molecules (or oil molecules) per droplet to vary at constant number of surfactant molecules (as has been treated in ref. (6)) and to allow variations of shape as treated in ref. (8).

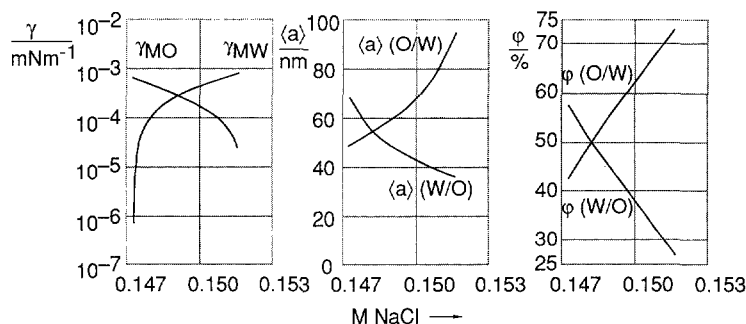


Figure 6. Interfacial tensions, average radii and volume fractions for Winsor I and Winsor II equilibria chosen in such a way that at the same overall composition $\phi(O/W) + \phi(W/O) = 1$. See also Table II.

Table II. Between 0.1472 and 0.1515 M NaCl at an oil composition of 19% pentanol+81% cyclohexane the same overall composition can be described as O/W (in equil. with O) or as W/O (in equil. with W). We give here: mol SDS adsorbed/l; the volume fractions and average radii of the droplets and the macroscopic interfacial tensions in the Winsor I and II equilibria.

M NaCl	mol SDS		<a>(O/W)		<a>(W/O)		γ_{MO}	γ_{MW}
	l	$\phi(O/W), \phi(W/O)$	nm	nm	nm	nm	mNm ⁻¹	mNm ⁻¹
0.1472	0.04265	42.6% 57.4%	48.97	67.57	0.00061	7×10^{-7}		
0.1475	0.0440	45.4% 54.6%	50.56	62.35	0.00055	0.000036		
0.148	0.0455	49.44% 50.56%	53.42	55.99	0.00046	0.000104		
0.150	0.0448	62.7% 37.3%	69.04	42.12	0.00017	0.00046		
0.151	0.0412	69.3% 30.7%	83.03	37.80	0.000069	0.00068		
0.1515	0.0383	73.0% 27.0%	94.45	35.84	0.000026	0.00081		

CONCLUSIONS

In conclusion we may state that the thermodynamic analysis of microemulsions developed in this and in previous papers gives a good qualitative description of droplet sizes, size distributions and interfacial tensions in Winsor type equilibria in their dependence on the amounts of water, oil and ionic surfactant and on the concentrations of salt and of cosurfactant. Even the quantitative agreement with experiments is not bad.

Here, especially the use of double layer theory for curved interfaces has been instrumental in explaining the salt influence (and indirectly, the influence of the cosurfactant). The theory can be and needs to be refined, especially aiming at a good model for bicontinuous, middle type microemulsions.

ACKNOWLEDGEMENTS

I thank Mrs. Marina Uit de Bulten for preparing the typescript and Mr. Jan den Boesterd for drawing and photographing the figures.

REFERENCES

1. A.A. Caljé, W.G.M. Agterof and A. Vrij, in "Micellization, Solubilization and Microemulsions", K.L. Mittal, Editor, Vol. 2, p. 779, Plenum Press, New York, 1977.
2. T.P. Hoar and J.H. Schulman, *Nature*, 152, 102 (1943).
3. G.J. Verhoeckx, P.L. de Bruyn and J.Th.G. Overbeek, *J. Colloid Interface Sci.*, 119, 409 (1987).
4. J.Th.G. Overbeek, G.J. Verhoeckx, P.L. de Bruyn and H.N.W. Lekkerkerker, *J. Colloid Interface Sci.*, 119, 422 (1987).
5. S.A. Safran, *J. Chem. Phys.*, 78, 2073 (1983).
6. M. Borkovec, H.-F. Eicke and J. Ricka, *J. Colloid Interface Sci.*, 131, 366 (1989).
7. J.Th.G. Overbeek, *Progress Colloid Polymer Sci.*, 83, 1 (1990).
8. J.C. Eriksson and S. Ljunggren, *Progress Colloid Polymer Sci.*, 81, 41 (1990).
9. H. Reiss, *J. Colloid Interface Sci.*, 53, 61 (1975); *Adv. Colloid Interface Sci.*, 7, 1 (1977).